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## Alum- $\text{Cs}_2\text{CO}_3$ as a New Recyclable Solid Base Catalyst for the Efficient Syntheses of Arylidenemalononitriles, Esters and Arylcinnamic Acids in Water

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The condensation between aromatic aldehydes and malononitrile, ethylcyanoacetate and malonic acid for the syntheses of arylidenemalononitriles, arylidenemalonic acid esters and aryl cinnamic acids in water using alum- $\text{Cs}_2\text{CO}_3$  as a solid support catalyst has been described. Alum- $\text{Cs}_2\text{CO}_3$  was found to be a highly active, stable and recyclable catalyst under reaction conditions.

**Keywords:** Alum- $\text{Cs}_2\text{CO}_3$ , Arylidenemalononitriles, Arylidene malonic acid esters, Aryl cinnamic acids, Water, Green approach.

### INTRODUCTION

Since Green chemistry is primarily concerned with the reduction of chemical hazards and pollution<sup>1</sup>. The use of environment friendly reagents and solvents in organic synthesis will be beneficial for both industry as well as for environment. Thus, the use of water as solvent in chemical reactions has proved to be a cleaner and safer alternative to organic solvents<sup>2</sup>.

Heterogeneous catalysis, which has the rapid and improved advantage of easy recoverability and recyclability and sometimes has further advantages of increased selectivity of the desired product over traditional homogeneous catalysis, is a key process in organic syntheses.

Various types of heterogeneous solid support catalysts have been employed so far. Recently, alum<sup>3</sup> has been proved as an efficient catalyst for Knoevenagel condensation due to its promising ability for C-C bond formation reactions<sup>4</sup>. Alum was also earlier used for the synthesis of various pharmaceutical intermediates like dihydropyrano[3,2-*b*]chromenediones<sup>5</sup>, arylidene-2,4-thiazolidinediones<sup>6</sup>, substituted coumarins<sup>3</sup>, pyrano[2,3-*d*]pyrimidinone and tetrahydrobenzo[*b*]pyran derivatives<sup>7</sup>, bis(indolyl)methanes<sup>8</sup> and also used for variety organic transformations such as Biginelli<sup>9</sup> and Pechmann<sup>3</sup> reactions. Various other catalysts were also employed for Knoevenagel reactions like  $\text{AlPO}_4\text{-Al}_2\text{O}_3$ ,  $\text{ZnCl}_2$ ,  $\text{LiBr}$ ,  $\text{CdI}$ ,  $\text{K}_3\text{PO}_4$ ,  $\text{Fe}_2(\text{SO}_3)_4$ ,  $\text{TiCl}_3(\text{SO}_3\text{CF}_3)$ ,  $\text{FeCl}_3$ ,  $\text{InCl}_3$ ,  $\text{RuCl}_3$  and lanthanum triflates<sup>10</sup>.

It was found that solid support catalysts like alum were found active when they treated with  $\text{Cs}_2\text{CO}_3$ . Without doubt, an alternative strategy for Knoevenagel reaction by this approach is worthwhile since it produces series compounds

which were useful intermediates for many pharmaceutical and biomedical industries. Arylidenemalononitriles were primarily used in the preparation of fine chemicals in agriculture and medicine fields as precursors of heterocycles with biological activity<sup>11</sup>. Whilst arylidene derivatives of ethylcyanoacetate were successfully employed in the synthesis of cyanocoumarins<sup>12</sup>, as antimetabolites<sup>13</sup>. Moreover, cinnamic acid derivatives have major applications in many fields such as in medicine as anticancer<sup>14</sup>, antituberculosis agents<sup>15</sup> and in industries as plasticizers, perfumes and aroma compounds<sup>16</sup> and as lubricants *etc.* There is a wide range of catalysts other than metal and solid supports were used for Knoevenagel condensation like modified hydrotalcites<sup>17</sup>, amines<sup>18</sup>,  $\text{K}_2\text{CO}_3$ <sup>19</sup>, Lewis-acid catalysts<sup>20</sup> and ionic liquids<sup>21</sup>.

The Knoevenagel condensation is strongly solvent dependent<sup>22,23</sup>. In addition, the use of aqueous and highly protic solvents is currently of great importance since it avoids problems of self-condensation, 1,2-elimination and retro-Knoevenagel reactions.

Herein, we report facile preparation of alum supported cesium carbonate (alum- $\text{Cs}_2\text{CO}_3$ ) and its effective application to the Knoevenagel condensation between different aromatic aldehydes and ethylcyanoacetate or malononitrile or malonic acid by stirring in water at 80-100 °C and also by using microwave irradiation technique. The products were obtained in high yield and purity.

### EXPERIMENTAL

All melting points are uncorrected and were obtained using open capillary tubes in sulfuric acid bath. TLC analysis was carried out on glass plates coated with silica gel-G and

spots were visualized using iodine or a UV lamp. IR spectra were recorded using Perkin-Elmer Model 46 instrument in KBr discs.  $^1\text{H}$  NMR were recorded in  $\text{CDCl}_3/\text{DMSO}$  using 400 MHz Varian Gemini spectrometer and mass spectra were recorded on LC-MS spectrometer, model HP-5989A. TGA was recorded on Perkin Elmer Pyris Diamond Thermal Analyzer in the temperature range 0-600 °C, with a heating rate of 10 K/s. XRD spectra from the ECA pressed samples were recorded by a rotating anode X-ray diffractometer (Rigaku 12 kW) with  $\text{Cu-K}\alpha$  radiation and a graphite monochromator, operating at 50 kV and 150 mA.

**Preparation of alum supported cesium carbonate (alum- $\text{Cs}_2\text{CO}_3$ ):** To a mixture of alum (3 g) and  $\text{Cs}_2\text{CO}_3$  (2.92 g) were grinded in a mortar using pestle for 10-15 min and the resulting compound washed with distilled water (10-15 mL). The reaction mixture was filtered, dried overnight at 100 °C and later at heating at 600-700 °C in a muffle furnace for 1 h.

**General procedure for synthesis of arylidene malononitriles, arylidene malonic acid esters and aryl cinnamic acids using alum- $\text{Cs}_2\text{CO}_3$ :** To a mixture of aldehyde (1 mmol), malononitrile or ethylcyano acetate or malonic acid (1 mmol) and distilled water (10 mL) in a round-bottom flask (50 mL), alum- $\text{Cs}_2\text{CO}_3$  (0.5 g) was added. The reaction mixture was allowed to heat on water bath at 100 °C for appropriate time (Table-1) with shaking regularly. The completion of the reaction was monitored by TLC. The reaction mixture was diluted with ethyl acetate and alum- $\text{Cs}_2\text{CO}_3$  was filtered off. The organic layer was separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The product was obtained after removal of the solvent under reduced pressure and recrystallized from ethanol. The catalyst was washed with distilled water (20 mL) and followed by ethyl acetate (15 mL) and dried 1 h at 100 °C for further use. The structures of the products were confirmed by IR,  $^1\text{H}$  NMR, mass spectral data and comparison with authentic samples.

**General procedure for microwave method using alum- $\text{Cs}_2\text{CO}_3$ :** To a mixture of aldehyde (1 mmol), malononitrile or ethylcyanoacetate or malonic acid (1 mmol), alum- $\text{Cs}_2\text{CO}_3$  (0.5 g) and distilled water (5 mL) in a 10 mL CEM-reaction tube sealed by rubber stopper and subjected to microwave irradiation for 5 min at 100 °C in the commercial micro-wave reactor. After that, the tube was cooled and the completion of reaction was checked by TLC. The reaction mixture was diluted with ethylacetate and alum- $\text{Cs}_2\text{CO}_3$  was filtered off. The organic layer was separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The product was obtained after removal of the solvent under reduced pressure and recrystallized from ethanol. The catalyst was washed with distilled water (20 mL) and followed by ethyl acetate (15 mL) and dried 1 h at 100 °C for further use. The structures of the products were confirmed by IR,  $^1\text{H}$  NMR, mass spectral data and comparison with authentic samples

## RESULTS AND DISCUSSION

Alum is an inexpensive, non-toxic, commercially available which is easily hand-able without any precautions. Equivalent amounts of alum and  $\text{Cs}_2\text{CO}_3$  were grinded in a mortar using a pestle for 15-30 min and washed it with double distilled water. The filtered solid was allowed to dry over night at 100 °C and later at 600-700 °C in a muffle furnace for 1 h. The characterization of alum- $\text{Cs}_2\text{CO}_3$  was done by TG-DTA, FTIR and X-ray diffraction analysis.

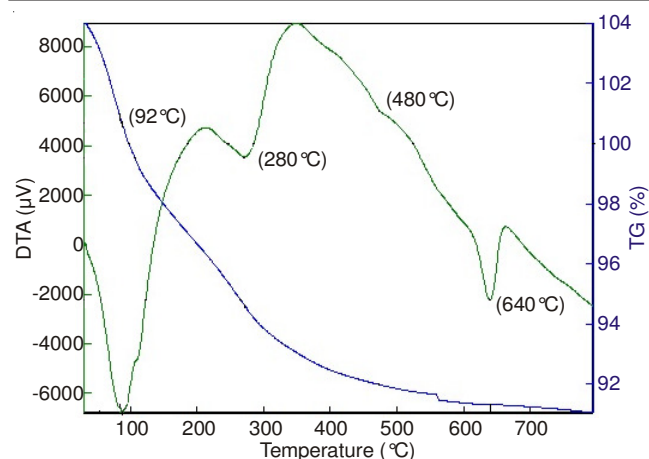
**TG-DTA analysis of alum- $\text{Cs}_2\text{CO}_3$ :** The TG-DTA analysis of alum- $\text{Cs}_2\text{CO}_3$  indicates that the material is degraded in five discrete steps mainly as shown in Fig. 1. The initial three degradations from 90-480 °C indicates the weight loss due to loss of moisture/or crystallization of water in three stages<sup>24</sup> (30-50 %) and the fourth effect with the dissociation of  $\text{KAl}(\text{SO}_4)_2$  and the formation of  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2\text{O}_3$ <sup>24</sup>. The fifth degradation at 630 °C indicates mass loss related to Cs. This weight loss can

TABLE-1  
ALUM- $\text{Cs}_2\text{CO}_3$  CATALYZED KNOVENAGEL CONDENSATION OF AROMATIC ALDEHYDES WITH MALONONITRILE AND ETHYLCYANOACETATE AT 80-100 °C AND IN m.w. METHOD AT 450 W FOR 3-5 min IN WATER

S. No.	Product <sup>a</sup> Ar = <b>3(a-q)</b>	X	Time (min)		Yield (%) <sup>b</sup>		m.p. (Lit. m.p) °C [Ref]
			At 100 °C	m.w.	At 100 °C	m.w.	
1.	<b>3a</b> - $\text{C}_6\text{H}_5$	CN	120	5	96	98	83-84 (82-83) Ref. [26]
2.	<b>3b</b> 4- $\text{OCH}_3$ - $\text{C}_6\text{H}_4$	CN	150	5	94	96	160-161(161) Ref. [26]
3.	<b>3c</b> 4- $\text{Cl}$ - $\text{C}_6\text{H}_4$	CN	120	4	90	90	77-78(77) Ref. [26]
4.	<b>3d</b> 4- $\text{OH}$ - $\text{C}_6\text{H}_4$	CN	180	4	94	90	135-136(134-135) Ref. [26]
5.	<b>3e</b> 3- $\text{NO}_2$ - $\text{C}_6\text{H}_4$	CN	120	5	92	94	160(159-160) Ref. [26]
6.	<b>3f</b> 3- $\text{OCH}_3$ - $\text{C}_6\text{H}_4$	CN	180	5	88	90	128-130(128) Ref. [26]
7.	<b>3g</b> 2- $\text{OH}$ - $\text{C}_6\text{H}_4$	CN	150	3	88	90	73-74(74) Ref. [26]
8.	<b>3h</b> 2-thiophenyl	CN	180	5	90	92	103-104(104) Ref. [26]
9.	<b>3i</b> 2-Furyl	CN	180	4	90	90	72-73(72) Ref. [10]
10.	<b>3j</b> - $\text{CH}=\text{CH}$ - $\text{C}_6\text{H}_5$	CN	180	5	96	90	126-127(126-129) Ref. [26]
11.	<b>3k</b> - $\text{C}_6\text{H}_5$	COOEt	180	5	94	94	49-50(49-52) Ref. [26]
12.	<b>3l</b> 4- $\text{Cl}$ - $\text{C}_6\text{H}_4$	COOEt	180	5	94	90	89-90(90-94) Ref. [26]
13.	<b>3m</b> 4- $\text{OH}$ - $\text{C}_6\text{H}_4$	COOEt	150	4	92	90	87-88(88-90) Ref. [26]
14.	<b>3n</b> 3- $\text{NO}_2$ - $\text{C}_6\text{H}_4$	COOEt	150	4	90	94	128-130(129-132) Ref. [26]
15.	<b>3o</b> 4- $\text{CH}_3$ - $\text{C}_6\text{H}_4$	COOEt	120	4	86	90	91-92(90-92) Ref. [26]
16.	<b>3p</b> - $\text{CH}=\text{CH}$ - $\text{C}_6\text{H}_4$	COOEt	120	5	88	92	112-114(114-115) Ref. [26]
17.	<b>3q</b> 2-Furyl	COOEt	120	5	90	90	94-95(94) Ref. [10]

<sup>a</sup>All the products were characterized by  $^1\text{H}$  NMR, IR and mass spectral data and comparison with the authentic samples available commercially or prepared according to the reported methods.

<sup>b</sup>Yields refers to the isolated yields.

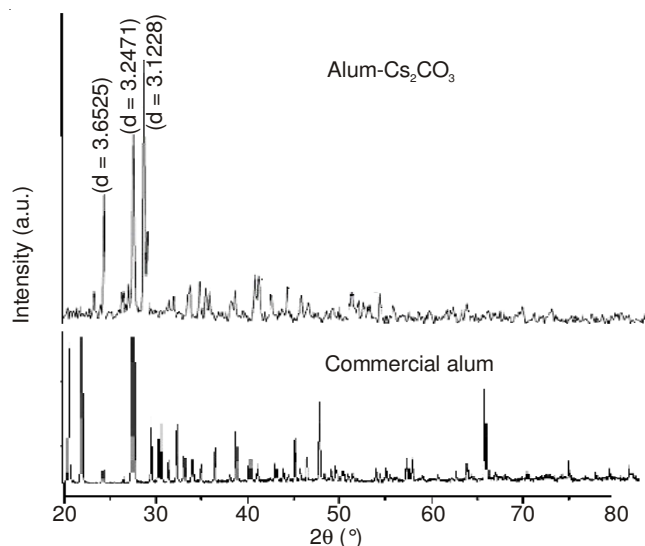
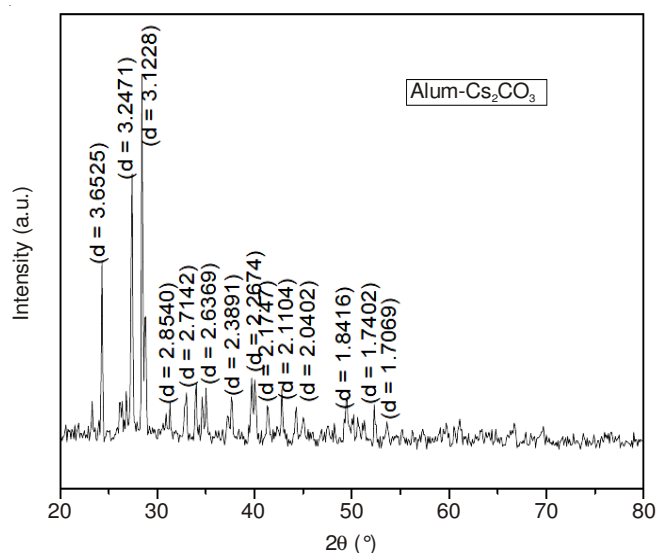
Fig. 1. TG-DTA of alum- $\text{Cs}_2\text{CO}_3$ 

be related to the release of carbon dioxide due to the precipitation of  $\text{CO}_3^{2-}$ . There is a complete degradation after 700 °C is due to  $\text{SO}_4^{2-}$  in nitrogen atmosphere. The TGA data indicated the high stability of alum- $\text{Cs}_2\text{CO}_3$  up to 700 °C (Fig. 1).

The FTIR of alum- $\text{Cs}_2\text{CO}_3$  has showed a weak absorbance at  $1610\text{ cm}^{-1}$  due to  $\text{CO}_3^{2-}$  and the tetrahedral  $\text{SO}_4^{2-}$  ion showed four bending vibrations at 981, 451, 1104 and  $613\text{ cm}^{-1}$ , respectively<sup>25</sup>.

**X-ray diffraction analysis:** The X-ray diffraction analysis of alum- $\text{Cs}_2\text{CO}_3$  indicates the crystalline nature of the catalyst. The diffractograms at different  $2\theta$  values indicates the presence of different mineral oxides present in the alum- $\text{Cs}_2\text{CO}_3$ . The X-ray analysis is interpreted by comparing with commercial alum data which indicates the modified structure of alum- $\text{Cs}_2\text{CO}_3$ . This data showed that, alum- $\text{Cs}_2\text{CO}_3$  when heated at high temperature, it is destroyed into  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2\text{O}_3$  which were represented by inter planar spacing values ( $2\theta$ ). The  $2\theta$  value at 3.6525 and 3.2471 indicates the presence of modified crystalline  $\text{K}_2\text{SO}_4$  and  $\alpha\text{-Al}_2\text{O}_3$ <sup>24</sup>. The  $2\theta$  value at 3.1228 related to cesium carbonate which was modified into fine hexagonal crystalline  $\text{Cs}_2\text{O}$ , which was absent in commercial alum X-ray data is a strong evident for successful catalyst preparation. The remaining diffractograms indicates the fine grained crystalline form of alum- $\text{Cs}_2\text{CO}_3$  (Fig. 2).

The Knoevenagel condensation between aromatic aldehydes and malononitrile or ethylcyanoacetate or malonic acid in the presence of catalyst alum- $\text{Cs}_2\text{CO}_3$  independently in double

Fig. 2. X-Ray diffractograms of alum- $\text{Cs}_2\text{CO}_3$  and comparison with commercial alum

distilled water was investigated. In order to optimize the reaction conditions, the condensation between malonic acid and *p*-chloro benzaldehyde was carried out with respect to different molar ratios of alum- $\text{Cs}_2\text{CO}_3$ , temperature, substrates and solvent.

TABLE-2  
SYNTHESIS OF ARYL CINNAMIC ACIDS **4(a-h)** USING MALONIC ACID AND ALDEHYDES

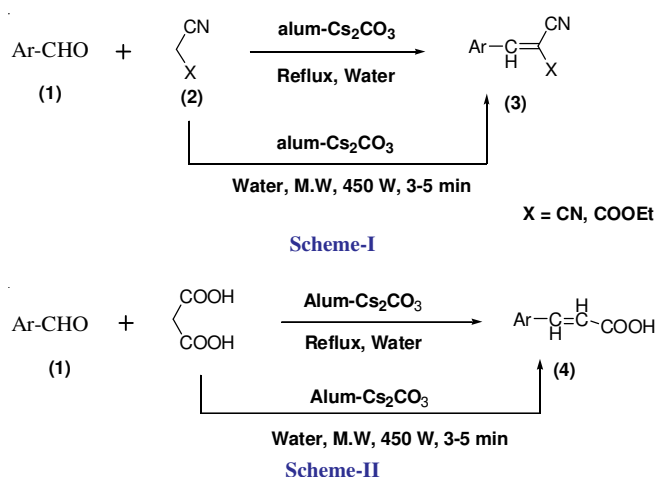
S. No.	Product <sup>a</sup> Ar = ( <b>4a-h</b> )	Time (min)		Yield (%) <sup>b</sup>		m.p (Lit. m.p) °C
		At 100 °C	m.w.	At 100 °C	m.w.	
1	<b>4a</b> ( $\text{C}_6\text{H}_5$ )	240	5	94	96	136-137 (135-136)
2	<b>4b</b> ( $\text{C}_6\text{H}_4\text{-}p\text{-Cl}$ )	180	4	92	94	245-247 (248)
3	<b>4c</b> ( $\text{C}_6\text{H}_4\text{-}p\text{-F}$ )	180	4	90	90	210-211 (209-210)
4	<b>4d</b> ( $\text{C}_6\text{H}_4\text{-}p\text{-CH}_3$ )	240	5	82	84	197-198 (196-198)
5	<b>4e</b> ( $\text{C}_6\text{H}_4\text{-}p\text{-NO}_2$ )	180	4	88	90	>250 (285)
6	<b>4f</b> (Piperonaldehyde)	210	5	80	86	242-244(243)
7	<b>4g</b> (Furfuraldehyde)	240	5	86	90	142-144(139-141)[50]
8	<b>4h</b> (Thiophene-2-aldehyde)	240	5	85	90	14-145 (145)[50]

<sup>a</sup>All the products were characterized by  $^1\text{H NMR}$ , IR and mass spectral data and comparison with the authentic samples available commercially or prepared according to the reported methods.

<sup>b</sup>Yields refers to the isolated yields.

*p*-Chlorobenzaldehyde and malonic acid were taken as sample test compounds. It was found that no reaction occurred between *p*-chlorobenzaldehyde and malonic acid in water at 100 °C. The same reaction was carried out with alum independently. After 12 h TLC indicated that the reaction had proceeded very slightly and, after workup, the product was isolated in only 2-5 % yield. Similar results obtained when the reaction was repeated with Cs<sub>2</sub>CO<sub>3</sub> (reaction time 24 h) and gave the isolated product in 5 % yield. As a consequence, when we carried out the reaction with alum-Cs<sub>2</sub>CO<sub>3</sub>, the amount of the catalytic systems needed was optimized with sample test substrates and with 0.2-0.6 g of the catalyst. It was found that 0.5 g of catalyst gave optimum results in terms of reaction time and yield (Table-2).

Secondly, the reaction with the test substrates was carried out at different temperatures (40, 60, 80 and 100 °C) and 100 °C was found to be the optimum reaction temperature. The same set of reactions were carried out in CEM-discovered microwave synthesizer at 450 W for 3-5 min and has got good results. A comparative study was carried out with K<sub>2</sub>CO<sub>3</sub> and CaCO<sub>3</sub>. These appear to be good catalysts but suffer from the disadvantages of low reaction rate and poor solubility in water. The amount of water as solvent was optimized with 5-10 mL of distilled water and it was found that 10 mL of water was sufficient to carry out the reaction in an efficient, mild and cost-effective way. Thus, the optimum conditions were established as: aldehyde (1 mmol), malonic acid (1 mmol), alum-Cs<sub>2</sub>CO<sub>3</sub> (0.5 g) and water (10 mL) at an optimum temperature of 100 °C and in microwave conditions at 450 W for 3-5 min. Under these conditions, product **4** (Table-2) was obtained in 96 % isolated yield after 2 h. This methodology was also applicable to heteroaromatic aldehydes and unsaturated aldehydes (**3h**, **3i**, **3q** & **3j**, **3p** Table-1). Promising better yields were obtained in 92, 90, 90 and 90, 92 % yields after 2-3 h respectively (Schemes I and II).



**Recoverability and reusability of the catalyst (alum-Cs<sub>2</sub>CO<sub>3</sub>):** To demonstrate the recyclability and reusability of alum-Cs<sub>2</sub>CO<sub>3</sub>, an intimate mixture of aldehyde (1 mmol), malonic acid (1 mmol) and alum-Cs<sub>2</sub>CO<sub>3</sub> (0.5 g) in water were refluxed at 100 °C about 3 h and after the completion of the reaction, ethyl acetate was added to the reaction mixture and the catalyst was recovered by filtration. The recovered alum-

Cs<sub>2</sub>CO<sub>3</sub> was thoroughly washed again with ethyl acetate and dried at 100 °C for overnight. This was be used for subsequent five fresh batches for the Knoevenagel condensation. It has been observed that the efficiency of the catalyst reducing little as the number times that it recovered from the reaction mixture. It also influencing on the reaction time and yield (Table-3, Fig. 3).

TABLE-3  
RECOVERABILITY AND REUSABILITY OF  
ALUM-Cs<sub>2</sub>CO<sub>3</sub> FOR THE SYNTHESIS OF **3**

S. No.	No. of the batches	Time (min)	Yield (%)
1	1 <sup>st</sup> batch	180	90
2	2 <sup>nd</sup> batch	180	90
3	3 <sup>rd</sup> batch	180	85
4	4 <sup>th</sup> batch	180	75
5	5 <sup>th</sup> batch	180	60
6	6 <sup>th</sup> batch	180	50

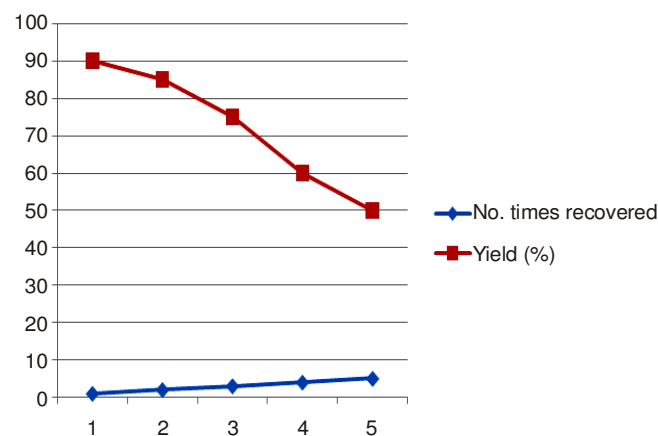
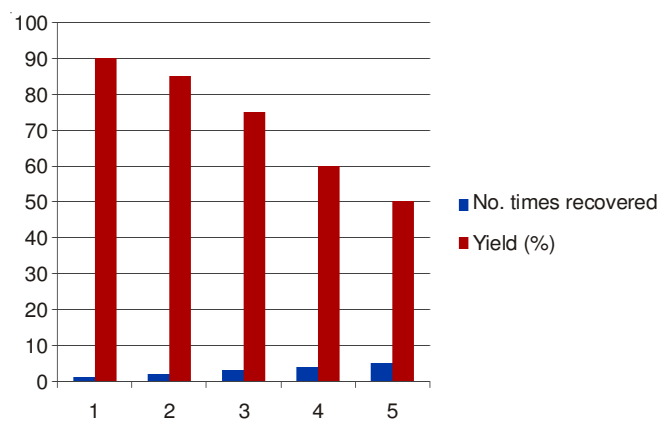


Fig. 3. Recoverability of alum-Cs<sub>2</sub>CO<sub>3</sub> and yield of **3(b)** graphical interpretation

## Conclusion

An efficient Knoevenagel condensations were achieved between a range of aromatic aldehydes and malonic acids or malononitriles or ethylcyanoacetates in short time periods by using alum-Cs<sub>2</sub>CO<sub>3</sub> as the catalyst and water as solvent under mild conditions both at refluxing temperature and microwave method. Due to its reusability, these catalysts are very efficient for C-C bond forming reactions.

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